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CHARACTERIZATION OF REACTION PRODUCTS IN A FLUID BED COAL COMBUSTION PROCESS BY THERMAL ANALYSIS

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MICROMEDIA

CHARACTERIZATION OF REACTION PRODUCTS IN A FLUID BED COAL COMBUSTION PROCESS BY THERMAL ANALYSIS

by

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ABSTRACT

Thermogravimetry (TG) was used to study representative samples from a fluid-bed coal combustion in which limestone is added to interact with evolving sulphur dioxide. Differential thermal analysis (DTA) was used concurrently with TG. Proximate analysis of the coal was also carried out by thermogravimetry. Thermal analysis of the samples in air and in argon indicated the presence of $Ca(OH)_2$ and minor amounts of $CaCO_3$ in the bed material, and coal, $CaCO_3$, $CaSO_4$ and $Ca(OH)_2$ in material collected from the baghouse dust. Useful information was obtained which may lead to a better understanding of the operation of the combustor.

ANALYSE THERMIQUE POUR LA CARACTÉRISATION DES PRODUITS DE COMBUSTION EN LIT FLUIDISÉ DU CHARBON

par

S.A. Mikhail

RÉSUMÉ

On a utilisé la thermogravimétrie (TG) pour l'étude d'échantillons types provenant de la combustion en lit fluidisé de charbon auquel du calcaire est ajouté pour favoriser la réaction d'échange avec l'anhydride sulfureux qui se dégage. On a utilisé l'analyse thermique différentielle (ATD) conjointement avec la thermogravimétrie (TG). On a aussi procédé à une analyse quantitative approximative du charbon au moyen de la thermogravimétrie. L'analyse thermique des échantillons dans un milieu composé d'air et d'argon a révélé la présence de $Ca(OH)_2$ et de quantités minimes de $CaCO_3$ dans le matériau du lit ainsi que de charbon, $CaCO_3$, $CaSO_4$, et $Ca(OH)_2$ dans le matériau provenant de la chambre de filtration. Il est possible que les renseignements recueillis lors de cette expérience puissent permettre de mieux comprendre le fonctionnement de la chambre de combustion.

INTRODUCTION

The effect of limestone addition on the reduction of the amount of sulphur emitted during a fluidized bed coal combustion process for power generation is currently being studied at Canada Centre for Mineral and Energy Technology (CANMET). Samples collected during the operation of a fluid-bed combustor using coal from Evans Coal Mines Limited, Nova Scotia, and limestone from Havelock Processing Limited, Havelock, New Brunswick, were submitted for study.* Proximate analysis of Evans coal was reported as 34.79% total volatiles, 10.7% ash and 54.51 fixed carbon. The combustor was operated at 850-900°C. Two of the samples were collected from the bed material and three from the baghouse dust where the particulate materials are collected from the effluent gases. Major components of the samples may include CaO, $CaSO_4$, ash and unreacted coal and $CaCO_3$.

PROCEDURE

The samples were studied by thermogravimetry (TG) in argon and in air flows using a heating rate of 20°/min. All TG experiments were conducted concurrently with differential thermal analysis (DTA) using a modified DuPont 1090 TA-951 TGA thermal analysis system. By using concurrent TG/DTA, various reactions were identified on the basis of weight changes as well as thermal effects. In this report, only the TG diagrams are presented.

RESULTS AND DISCUSSION

In preliminary experiments, Evans coal was subjected to proximate analysis to determine the moisture content, volatile matter, fixed carbon and ash content. Using thermogravimetry for proximate analysis, the sample is heated in argon up to 900°C. The observed weight loss around 100°C represents the moisture content and the weight loss up to 900°C the total

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*Samples were submitted by V. Razbin and R.K. Jeffery, Energy Research Laboratories, CANMET.

volatiles. Isothermally at 900°C, air is introduced to react with carbon and evolve as CO_2 causing a weight loss that represents the constituent fixed carbon. The ash content is represented by the final weight of the sample. The analysis of the coal indicated the presence of about 3% moisture, 32% volatiles, 53.5% fixed carbon and 11.5% ash.

Samples of material taken from the bed were also subjected to the procedure used for proximate analysis and the resulting TG diagrams, Figures 1 and 3, indicated a weight loss of about 8.5% at 400°C and another weight loss of about 1% at 600°C. No further weight loss was observed when air was introduced at 900°C which indicated the material had no carbon in it. The first weight loss, around 400°C, is typical of the dehydration of $Ca(OH)_2$. The second weight loss is characteristic for the decomposition of $CaCO_3$. For verification, reagent grade $Ca(OH)_2$ was heated in an argon flow and the resulting thermal diagram was very similar to that of the bed material including the second weight loss at 600°C. This result indicated that the hydrate contained minor amounts of $CaCO_3$ which may have originated from the interaction with atmospheric CO_2 during storage. Samples of material taken from the bed were also examined in an air flow and the TG diagrams, Figures 2 and 4, showed fairly similar patterns to those produced in argon; a weight loss of 6-7% around 400°C and another weight loss of 1-2% around 600°C. The slight decrease in the first weight loss and the slight increase in the second may indicate that, in samples heated in air and hence exposed to CO_2, more carbonation of the hydrate occurred. Estimates can be made of the mass % of $Ca(OH)_2$ and $CaCO_3$ in these samples from the results of TG in argon. The $Ca(OH)_2$ undoubtedly formed by hydration of CaO in the samples during storage and handling, since CaO is the product expected from calcination of $CaCO_3$. The $CaCO_3$ detected in the samples may not be residual uncalcined limestone, but may have resulted from reaction of $Ca(OH)_2$ with CO_2 from the atmosphere.

The baghouse dust samples, in air, Figures 5, 7 and 9, showed a weight loss of 7-9% around 500°C and another weight loss of 9-10% around 650°C. In these samples, combustion of unreacted coal may account for the first weight loss (concurrent DTA showed a large exothermic effect) and decomposition of unreacted calcium carbonate to calcium oxide and CO_2 for the second weight loss (concurrent DTA showed an endothermic effect characteristic for the decomposition of calcium carbonate).

In argon, the baghouse dust samples, Figures 6, 8 and 10, showed a weight loss of about 1% around 400°C indicating the presence of some $Ca(OH)_2$ in the samples. Three, partially overlapping, stages of weight loss were also recorded. The first, 4-5%, started around 575°C, the second, about 12%, started around 675°C and the third started around 850°C and continued beyond the end of the run, around 1050°C. Besides the evolution of coal volatiles, possible reactions leading to weight losses in this temperature range are the following:

$$CaCO_3 \longrightarrow CaO + CO_2 \qquad (1)$$

$$CaSO_4 + 2C \longrightarrow CaS + 2CO_2 \qquad (2)$$

For verification, the two reactions were examined separately by thermogravimetry using reagent grade materials. Reaction 1 was found to take place at 650-700°C yielding a weight loss of 42% (theoretical value: 44%) and reaction 2 was found to start around 850°C yielding a weight loss of 53.2% (theoretical value: 55%). The differences between the experimental and the theoretical values may be due to impurities in the starting materials. The identitites of the solid products of the two reactions were confirmed by X-ray diffraction analysis. The solid product of reaction 2 was also found to contain minor amounts of CaO which may point to a reaction such as:

$$2CaSO_4 + C \longrightarrow 2CaO + CO_2 + 2SO_2 \qquad (3)$$

Based on these results, a mixture of reagent grade compounds $CaCO_3$, $CaSO_4$, $Ca(OH)_2$, SiO_2 (as a diluent) and Evans coal previously heated in argon up to 500°C was examined by thermogravimetry in an argon flow. The reason for the coal pretreatment was to simulate the actual situation inside the fluid-bed reactor in which the unreacted coal, during its passage through the reaction zone (850-900°C), may have attained a fairly high temperature (probably 400-500°C) at which some of its constituent volatiles were lost. The TG diagram of the mixture is shown in Figure 11. From the close similarity between this diagram and the diagrams of the baghouse dust samples, Figures 6, 8 and 10, it seems reasonable to conclude that the latter samples contained the same active components found in the

mixture, namely $CaCO_3$, $CaSO_4$, $Ca(OH)_2$ and coal. Other "inactive" reaction products such as ash or any CaO not hydrated during storage, which had been generated in the reaction zone of the fluid-bed combustor, may also be present in the samples and act as diluents. A semi-quantitative assessment of the amounts of the active components may be done by comparing the TG diagrams of the baghouse dust samples to that of the mixture which contained 30% coal, 26% SiO_2, 24% $CaCO_3$, 12% $CaSO_4$ and 8% $Ca(OH)_2$. Caution must be exercised in any assessment, however, because temperature regions for the reactions showing weight loss appear to exhibit significant overlap. When a coal sample was heated in argon, the evolution of volatiles started around 380°C and continued steadily until the end of the experiment, at 1050°C. It is also noticeable from the TG diagrams in Figures 6, 8 and 10 that the decomposition of the limestone in the baghouse samples in argon occurs in a higher temperature range (ending at 860-870°C) than that in the mixture (ending at about 820°C, Figure 11). In air, decomposition of the limestone in the baghouse samples occurs in an even lower temperature range (ending at 710-720°C). These differences may be due to formation of a carbonaceous coating on the surface of the limestone particles during evolution of volatile organic material or during partial fusion of organic material under an inert atmosphere. This coating may inhibit escape of CO_2 from the limestone praticles and create locally high partial pressures of CO_2.

CONCLUSION

Useful information concerning the presence of residual coal, limestone, $CaSO_4$ and $Ca(OH)_2$ (from hydration of CaO) in samples collected from a fluid-bed coal combustor chamber to which limestone has been added for SO_2 capture can be obtained from TG studies conducted in air and in argon. However, the proximate analysis procedure using TG, which works well for a normal coal sample, does not give results that can be interpreted in the conventional way when applied to baghouse samples. Quantitative interpretation of the results may be complicated by overlapping temperature ranges for weight losses due to different reactions, and it is essential that interpretation of the TG results should be done with a knowledge of the processes giving rise to weight losses in different temperature regions and under different atmospheres.

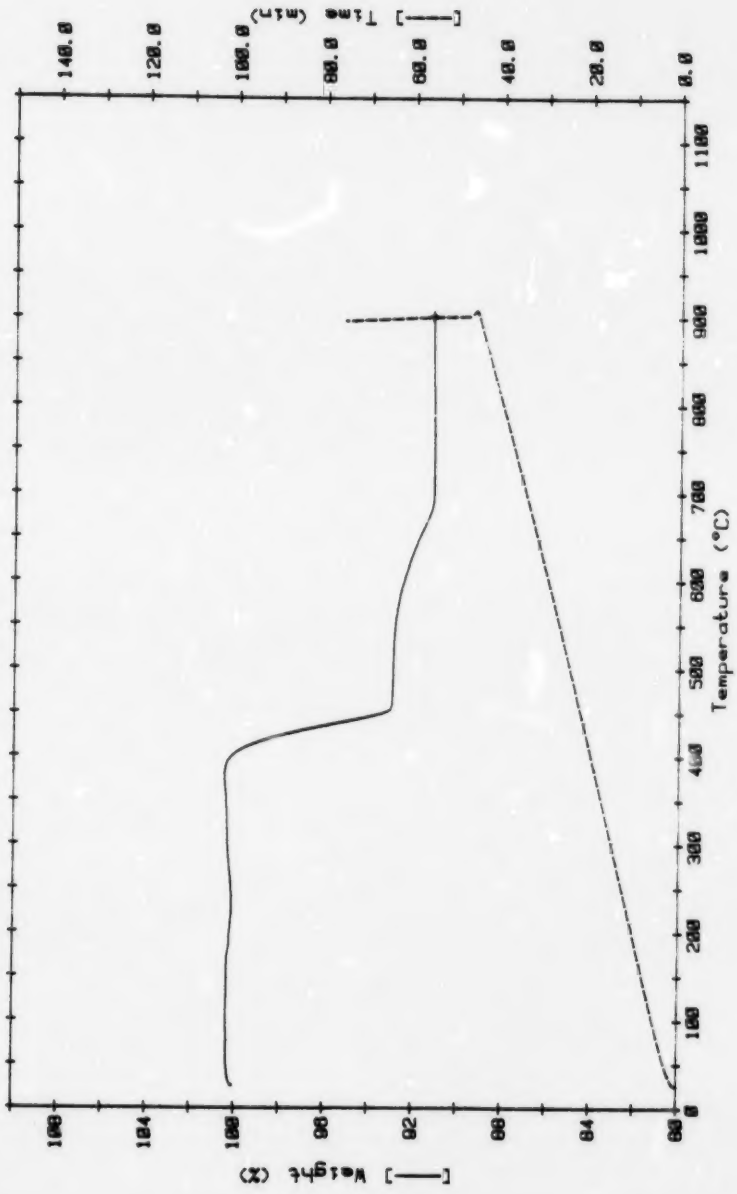

Fig. 1. TG diagram for fluid-bed material sample No. A650-83 in argon up to 900°C then in air

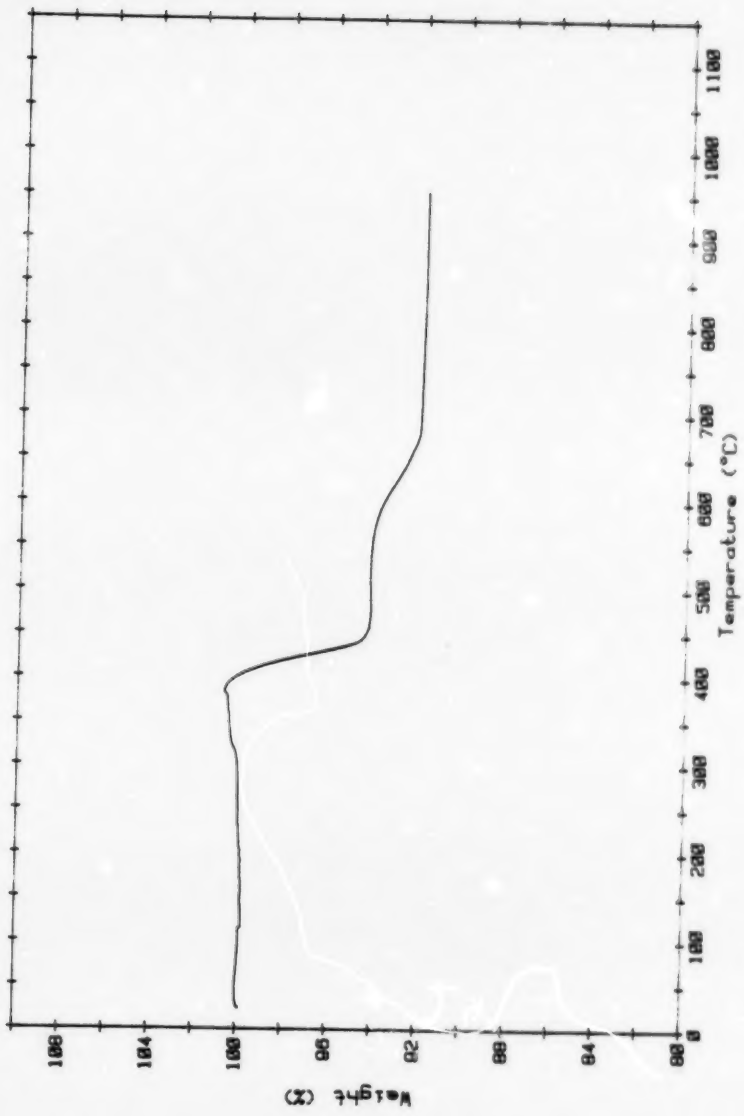

Fig. 2. TG diagram for fluid-bed material sample No. A650-83 in air

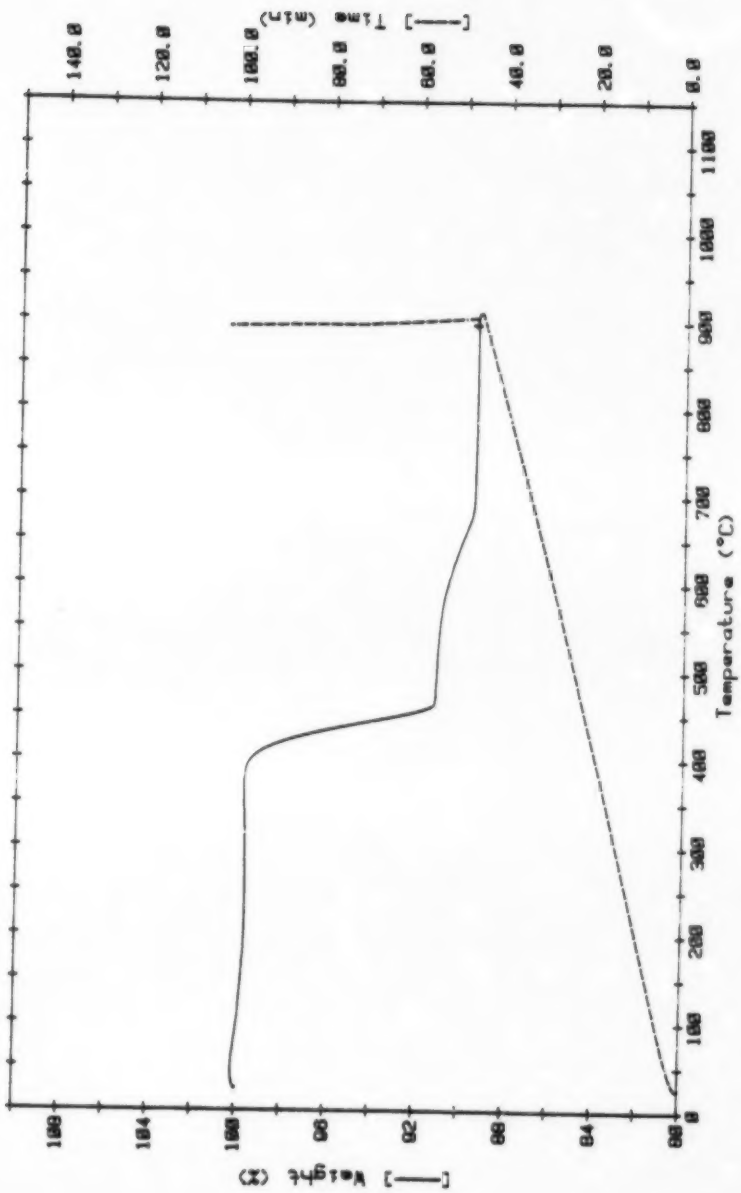

Fig. 3. TG diagram for fluid-bed material sample No. A653-83 in argon up to 900°C then in air

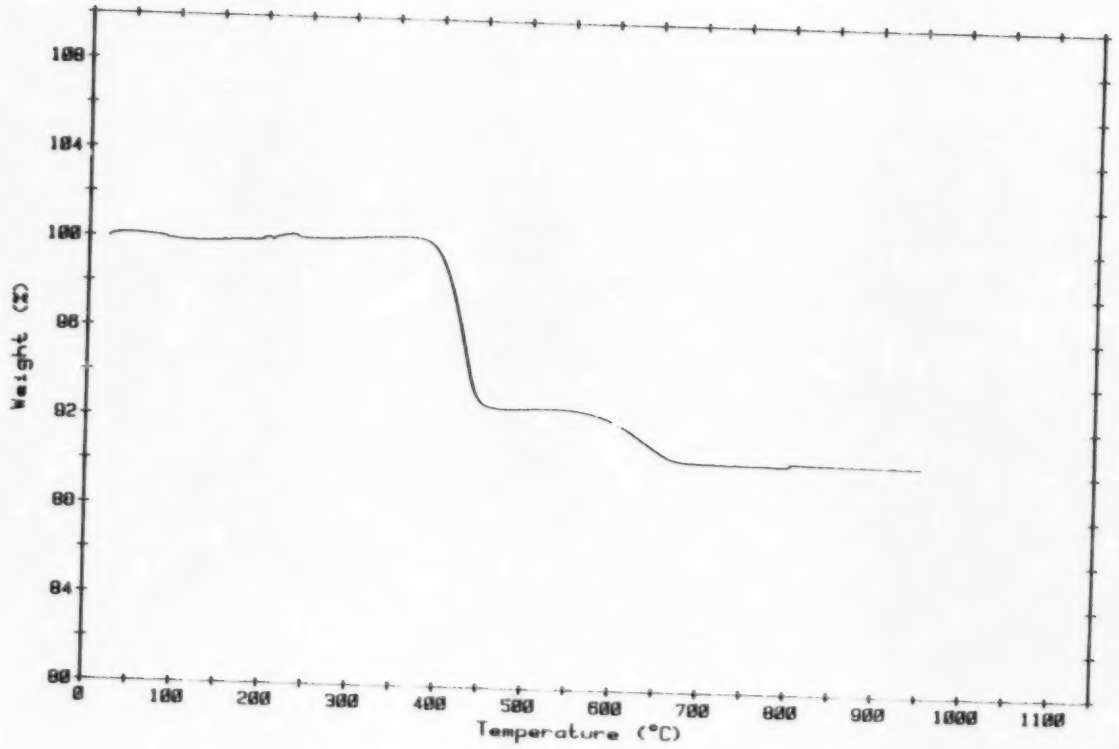

Fig. 4. TG diagram for fluid-bed material sample No. A653-83 in air

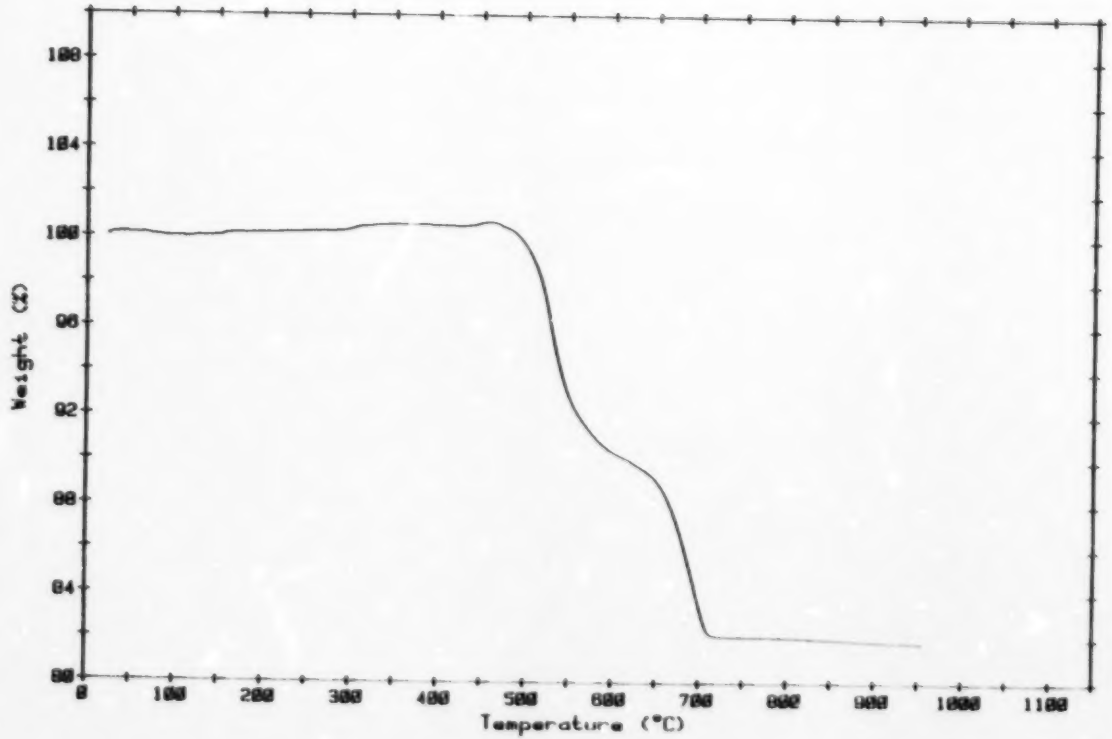

Fig. 5. TG diagram for baghouse material sample No. A654-83 in air

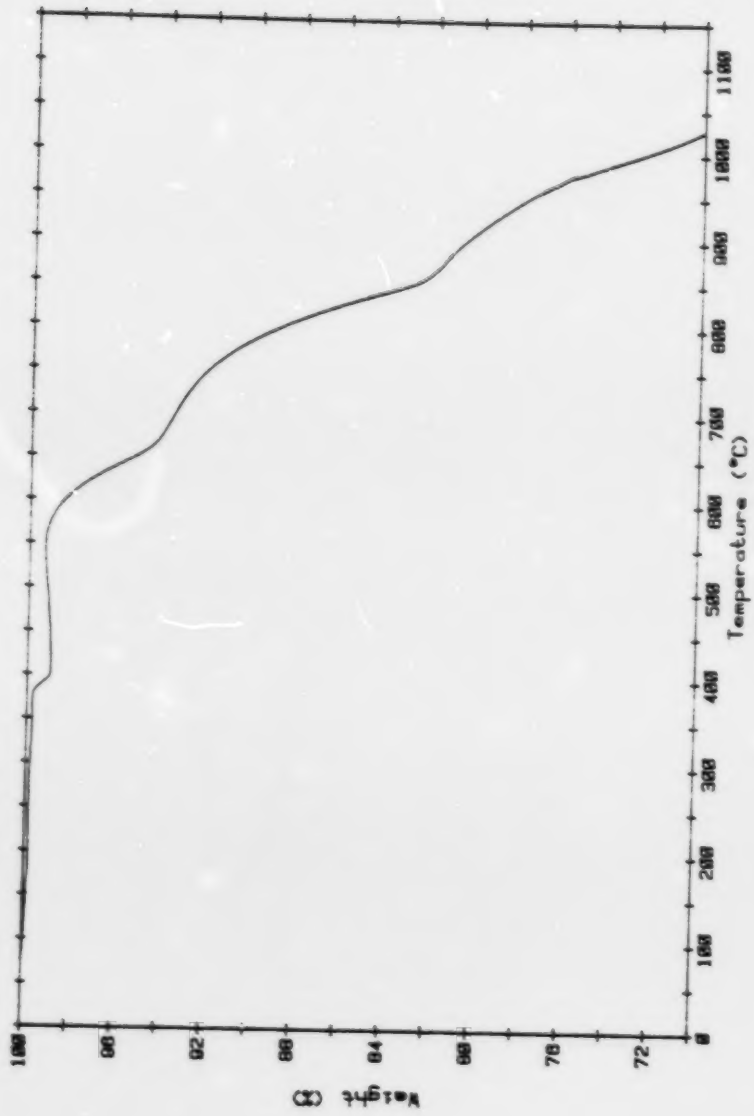

Fig. 6. TG diagram for baghouse material sample No. A654-83 in argon

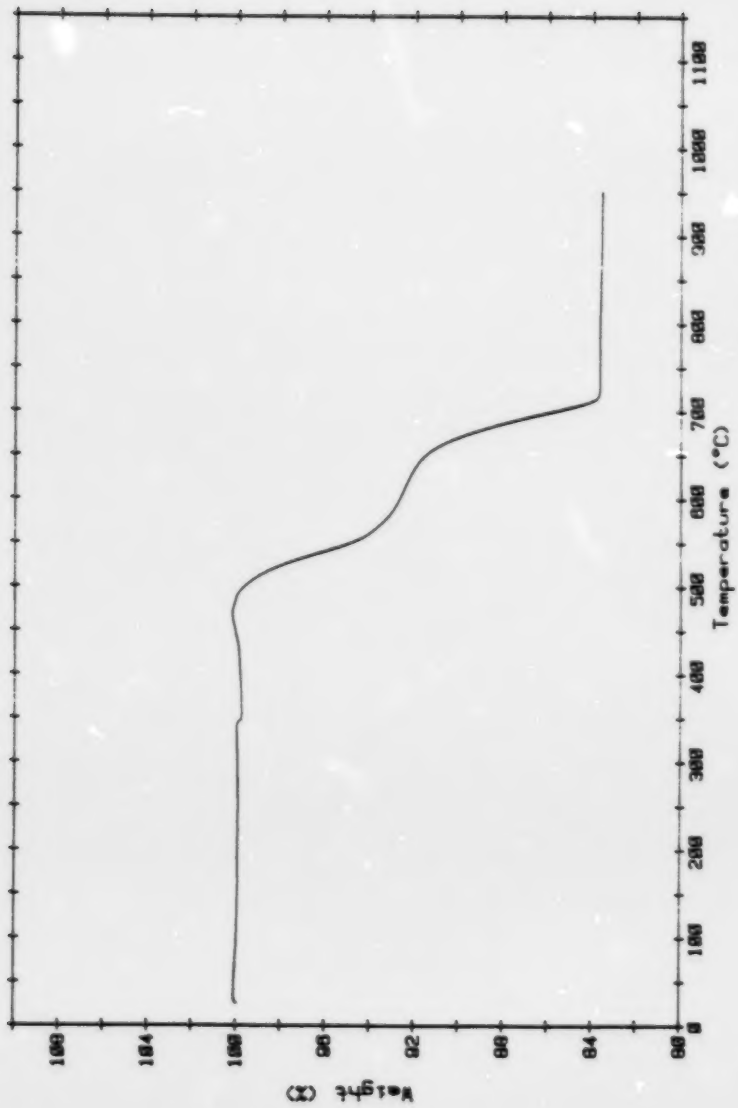

Fig. 7. TG diagram for baghouse material sample No. A655-83 in air

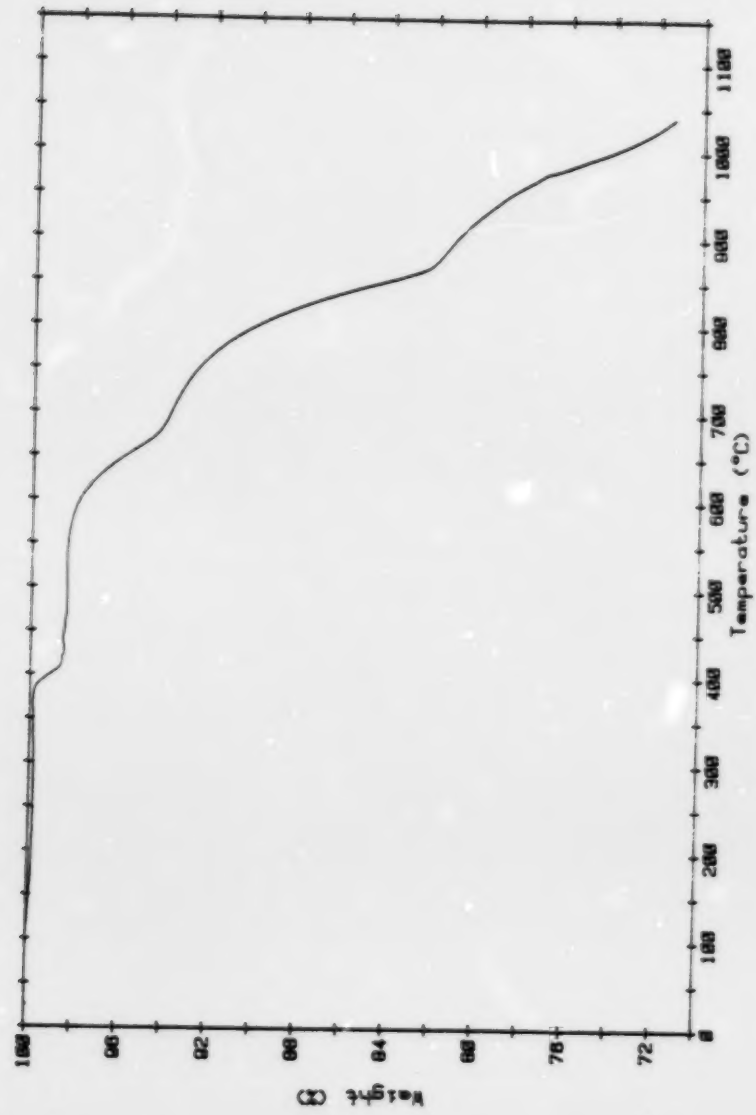

Fig. 8. TG diagram for baghouse material sample No. A655-83 in argon

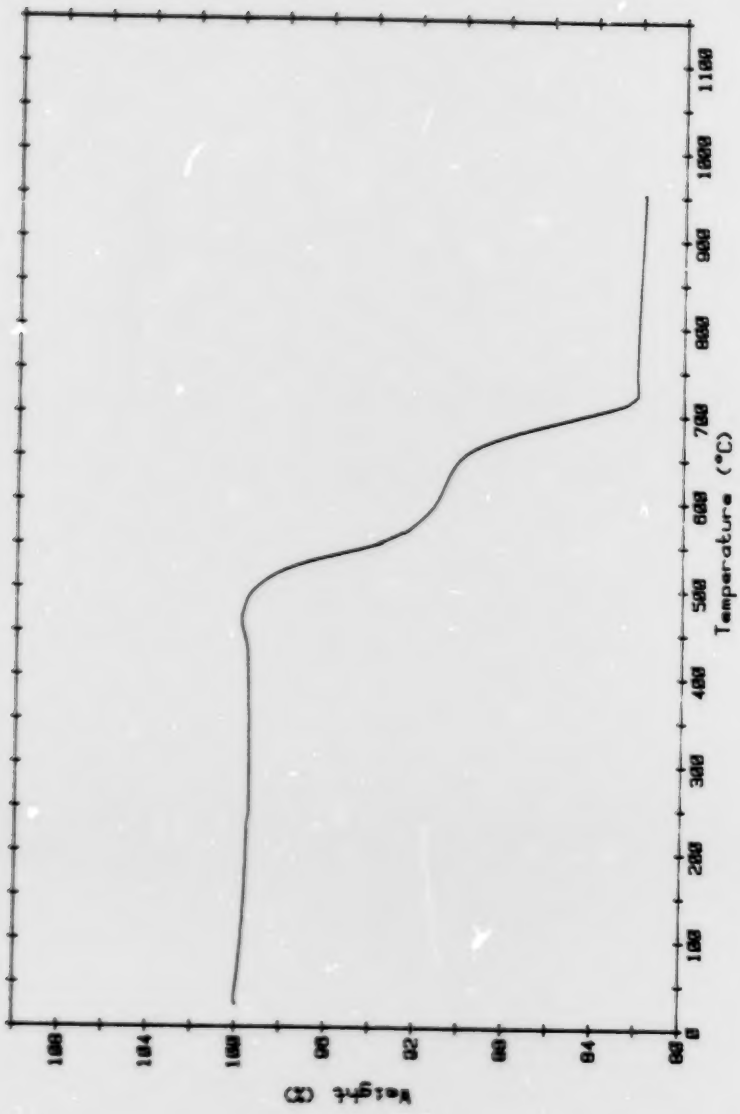

Fig. 9. TG diagram for baghouse material sample No. A656-83 in air

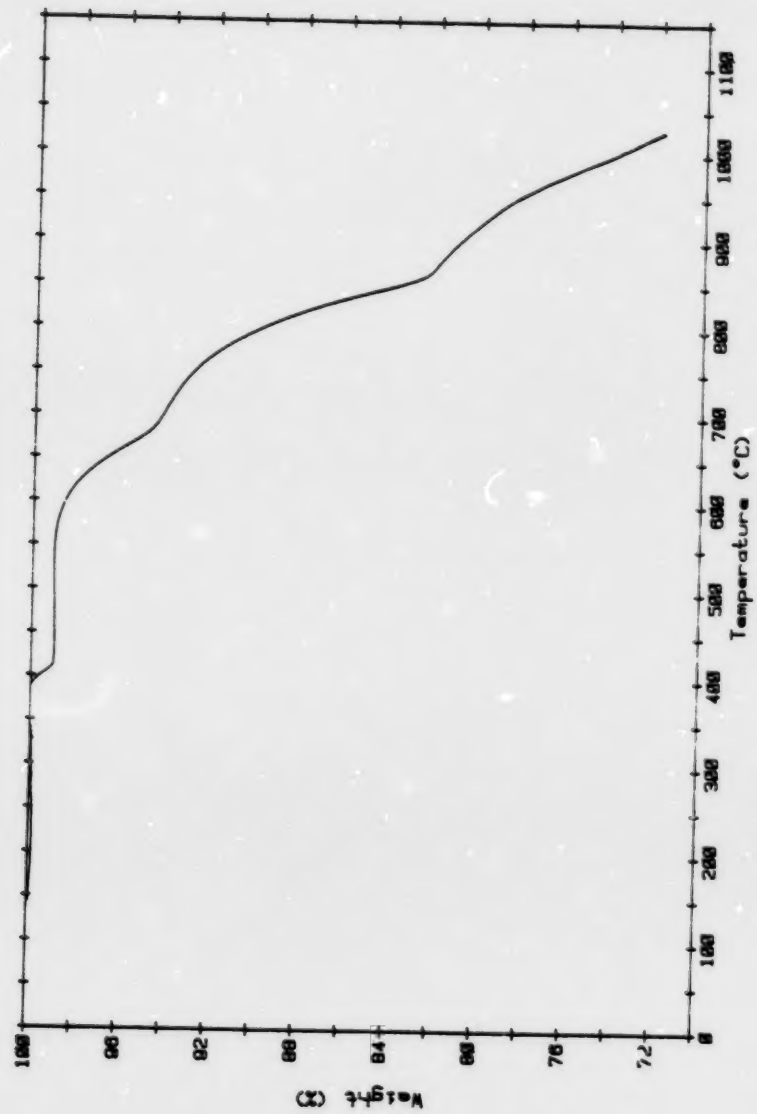

Fig. 10. TG diagram for baghouse material sample No. A656-83 in argon

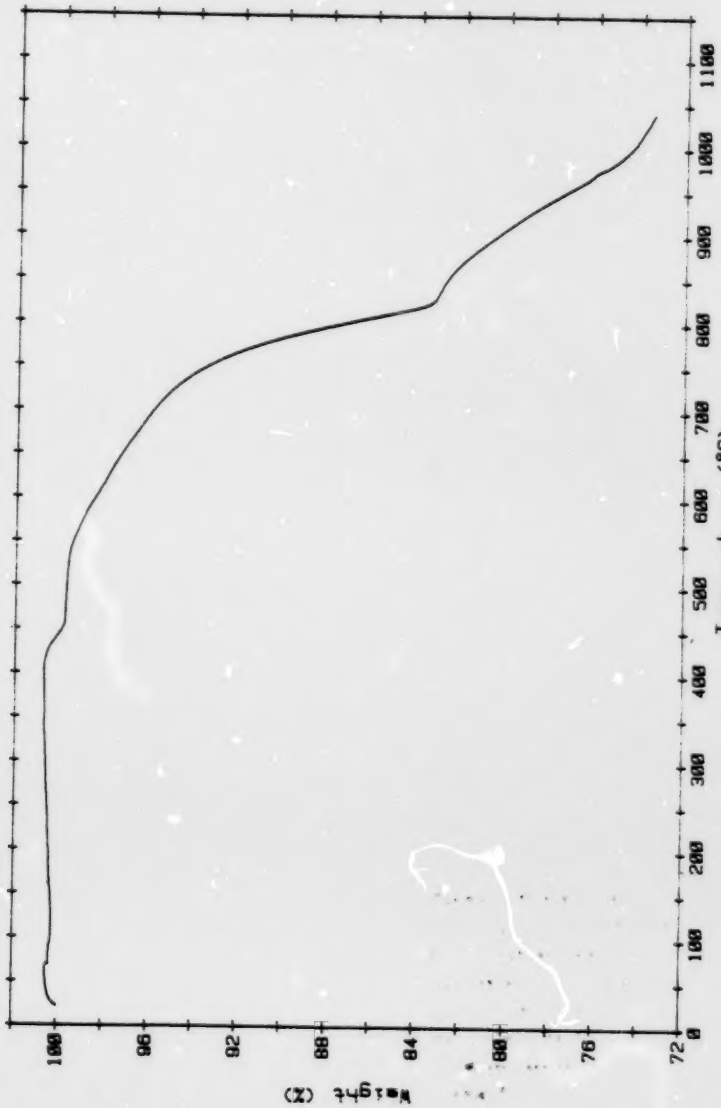

Fig. 11. TG diagram for a mixture of 30% coal, 24% $CaCO_3$, 12% $CaSO_4$, 8% $Ca(OH)_2$ and 26% SiO_2 in argon